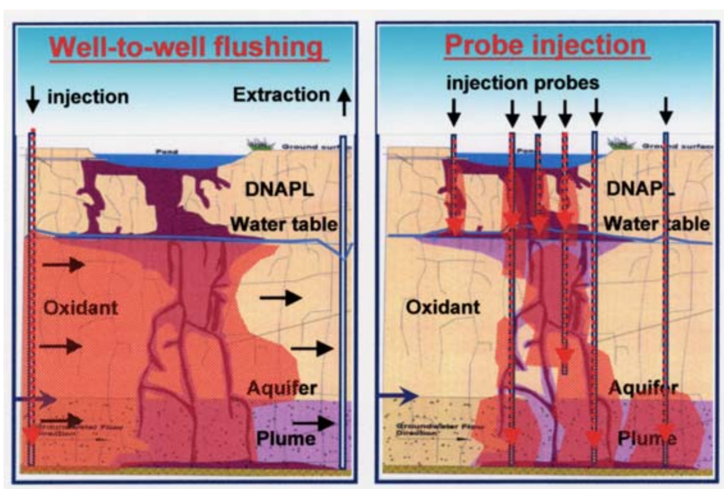
# In Situ Chemical Oxidation for Remediation of Contaminated Groundwater

## *Frequently Asked Questions*

**An information guide prepared in support of ESTCP Project ER-0623 sponsored by the Environmental Security Technology Certification Program**

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# Contents

# Preface

This document contains a set of frequently asked questions (FAQ) along with short answers concerning the application of in situ chemical oxidation (ISCO) for remediation of contaminated groundwater. This FAQ guide is designed to provide an overview of the principles and practices of in situ chemical oxidation (ISCO) for remediation of groundwater. The intended audience includes DoD Remedial Project Managers (RPMs), but the document is also well suited for site owners/managers in general. Readers are assumed to have a general understanding of site characterization/assessment and remediation technology selection and applications (i.e., this FAQ guide is not intended for someone new to the field of contaminated sites and remediation).

This FAQ guide was prepared as part of ESTCP Project ER-0623: *"In Situ Chemical Oxidation for Groundwater Remediation – Technology Practices Manual"*. The goal of ER-0623 is to help advance the standard-of-practice of ISCO and enable more predictable, cost-effective application at DoD sites by providing knowledge and know-how within a comprehensive technology practices manual (TPM). The core elements of the TPM are provided on this CD and include:

- Principles and processes of ISCO for groundwater remediation, which provides a critical review of the literature to document the state-of-science for each of several oxidants covering their reaction chemistries along with their transport/fate in the subsurface (see S1. Literature Summary and S2. Annotated Literature Review);
- Field applications and experiences with ISCO, which provides a compilation and critical analysis of ISCO field site case histories in extended narrative form as well as through a database for ISCO, referred to as DISCO, which can be queried based on site-specific conditions and ISCO performance goals (see Database of Field Applications and Experiences with ISCO Sites);
- An ISCO Protocol, which is a decision-making framework that includes logic diagrams with key decision aids and modeling tools for site-specific screening, conceptual design, detailed design and planning, and performance monitoring (see the E-Protocol Index); and
- A FAQ guide containing a set of basic questions along with short responses. This FAQ guide refers extensively to the other elements of the TPM, particularly the case history data and lessons learned through analysis of the DISCO database information and statistical outcomes.

Many individuals contributed to preparation of this FAQ guide. The list of questions was developed by members of the ER-0623 project team and the responses were prepared based on the results of the other core elements of the overall ER-0623 project. Michelle Crimi (Clarkson University) served as lead author with input provided by Bob Siegrist (Colorado School of Mines), Ben Petri (Colorado School of Mines), Fritz Krembs (Aquifer Solutions), Tom Simpkin (CH2MHILL), and Tom Palaia (CH2MHILL). Mike Singletary (NFECSD), Nancy Ruiz (NFESC), and Val Jurka (NFESC) completed reviews and provided valuable comments on an earlier draft version of the FAQ guide.

The ESTCP Project ER-0623 was sponsored by the DoD Environmental Security Technology Certification Program. Dr. Andrea Leeson, Program Manager, and other ESTCP staff are gratefully acknowledged for their assistance and support.

# Introduction

Among the technologies used to remediate contaminated sites, in situ chemical oxidation (ISCO) is often considered and utilized to clean up organic chemical contamination in subsurface source zones and/or associated groundwater plumes. A wide variety of organic contaminants in soil and groundwater have been treated with several different chemical oxidants including permanganate, catalyzed hydrogen peroxide, ozone, persulfate, peroxone, and percarbonate (see table below). For ISCO, these oxidants have been introduced into the subsurface through an assortment of delivery approaches commonly including networks of injection wells or direct push probes.

Full-scale ISCO deployment has been accelerating, but only well-planned ISCO implementations will achieve performance goals in a cost-effective manner while avoiding unforeseen adverse effects. Understanding ISCO and matching the oxidant and delivery system to the contaminants of concern and the subsurface conditions at a particular site remains critical to achieving performance goals.

During the past decade, laboratory research has continued to elucidate the science of ISCO, and technologies for field implementation have been developed and refined. Concurrently, field applications of ISCO have yielded practical insights regarding system engineering and performance capabilities, leading to an evolving standard-of-practice for ISCO screening, design, implementation, and performance monitoring.

The intent of this document is to provide a concise overview of ISCO applicability, design, implementation, and performance for groundwater remediation in the form of "Frequently Asked Questions". The questions included in this document are those that appear to be most commonly asked by, and likely to be most useful to, remedial project managers (RPMs) and similar constituencies. A total of 25 questions are included in this guide, categorized under the ISCO process headings of "ISCO at a Glance", "ISCO Screening", "ISCO Conceptual Design", "ISCO Detailed Design and Planning", and "ISCO Operation and Performance Monitoring".

As presented in this FAQ guide, each of 25 questions is followed by a brief and focused response. Further detailed information concerning each question is contained in the ISCO Technology Practices Manual.

**Oxidants can differ in their form, reactive species, and activation**

| Oxidant | Commercial Form | Primary Reactive Species[1] | Activation |
|---|---|---|---|
| Permanganate | powder or liquid | $MnO_4^-$ | none |
| Catalyzed $H_2O_2$ | liquid | $\bullet OH$ $\bullet O_2^-$ $\bullet HO_2$ $HO_2^-$ | none, Fe(II) |
| Ozone | gas | $O_3$ $\bullet OH$ | none |
| Persulfate | powder | $SO_4^{2-}$ $\bullet SO_4^-$ | none, Fe(II), heat, $H_2O_2$, high pH |
| Peroxone | liquid and gas | $O_3$ $\bullet OH$ | $H_2O_2$ |
| Percarbonate | powder | $\bullet OH$ | Fe(II) |

[1]Oxidizing power of different reactive species (electrode potential in volts): **$MnO_4^-$** = permanganate anion (1.7V); **$\bullet OH$** = hydroxyl radical (2.8V); **$\bullet O_2^-$** = superoxide radical (-2.4V); **$\bullet HO_2$** = perhydroxyl radical (1.7V); **$HO_2^-$** = hydroperoxide anion (-0.88V); **$O_3$** = ozone (2.1V); **$SO_4^{2-}$** = persulfate anion (2.1V); **$\bullet SO_4^-$** = sulfate radical (2.6V)

Source: Modified from Huling and Pivetz 2006

# ISCO at a Glance

## 1. What is ISCO and how does it work?

ISCO involves the introduction of a chemical oxidant into the subsurface to react with contaminants of concern (COCs) to convert them into less harmful products. Oxidative degradation can occur through electron transfer processes (gain or loss of electrons resulting in transformation) using permanganate and un-activated persulfate, or through generation (via use of activating chemicals or materials) of free radical species (highly reactive chemical entities with unpaired electrons) in the case of activated persulfate and catalyzed hydrogen peroxide. Ozone reactions can occur through both electron transfer and free radical formation.

**Common oxidants and frequently targeted COCs:**

- Catalyzed hydrogen peroxide
  - Most contaminants are amenable including chlorocarbons, fuel hydrocarbons, pesticides, PAHs
- Permanganate
  - Chloroethenes and PAHs
- Ozone
  - Fuel hydrocarbons and PAHs
- Activated persulfate
  - Chlorocarbons and fuel hydrocarbons

**Achieving COC degradation:**

Achieving a treatment goal using ISCO requires 1) matching an oxidant to the COCs and site conditions and 2) using an effective delivery approach to distribute oxidant throughout a target treatment zone (TTZ) and sustain adequate concentrations for a sufficient period of time so oxidation of the COCs can occur.

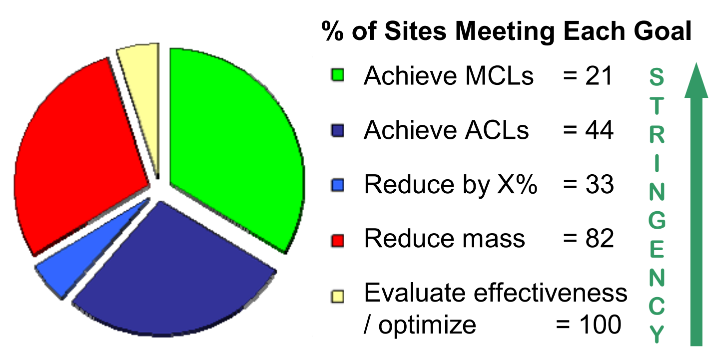
## 2. What treatment goals can ISCO achieve?

A properly designed ISCO system that achieves effective contact (i.e., mixing) of the right oxidant with the COCs can remediate contaminated groundwater to common treatment goals (e.g., 99.9% reduction in concentration). However, as of this writing, remediation of DNAPL source zones by ISCO alone to USEPA MCLs in groundwater (e.g., TCE = 5 ppb) has not been documented. Therefore, for DNAPL source zones where cleanup goals are stringent, ISCO is typically implemented in a treatment train approach where ISCO is combined with pre-ISCO treatments such as DNAPL extraction techniques and/or post-ISCO treatments such as enhanced reductive dechlorination or monitored natural attenuation.

**ISCO treatment goals:**

The pie chart shows how frequently specific goals have been set for sites included in a review of ISCO case histories as part of this project (ER-0623). MCLs (most stringent) are the goal most frequently set for sites. However, as shown by the % listed, MCLs have been achieved with a lower frequency than other less stringent goals.

**Site distribution by goal set:**



# 3. What are the potential positive and negative attributes of ISCO?

All remediation technologies have potential advantages and disadvantages depending on site conditions, contaminant conditions, and clean-up goals. ISCO has the same potential advantages and disadvantages that are inherent to in situ remediation technologies as well as some that are unique to chemical oxidation.

**Potential positive attributes of ISCO:**

- Robust treatment method.
- Can be implemented quickly.
- Variety of oxidants and activation approaches.
- Variety of delivery approaches.
- Applicable to a range of subsurface conditions.
- Relatively low mobilization costs.
- Ability to couple with pre- and post-treatment methods synergistically.
- Well-accepted by the regulatory community in many areas.

**Potential negative attributes of ISCO:**

- Potential need for large amounts of chemicals.
  - Unproductive oxidant consumption due to reaction with natural media (natural oxidant demand (NOD)). Fast reaction rates can limit oxidant transport.
- Resistance of some COCs to oxidation.
- Limited ability to penetrate low permeability soil and groundwater zones.
- Potential for ISCO-induced effects (e.g., gas evolution, permeability reduction, secondary water quality effects).
- Potential for rebound of target COCs.
- Inability to treat DNAPL source areas to MCLs.

# 4. Is ISCO an established remedy with a clear standard of practice?

ISCO has become an established remedy that should be seriously considered for sites where organic chemicals in groundwater have been determined to be the COCs and remediation is required to meet risk-based clean up goals. It is now recognized that there are key questions that must be carefully considered and addressed during selection, design, and implementation of an ISCO system at a particular site. However, details of how this is accomplished vary from site to site, and there is not yet a clear, widely accepted standard of practice.

**An evolving standard of practice for ISCO:**

- ISCO has evolved during the past decade and advancements and innovations in ISCO science and technology are continuing.
- There is not yet a detailed, widely accepted standard of practice for the application of ISCO to remediate a particular contaminated site.
  - ISCO practices continue to vary and depend on the knowledge and experience of the professionals responsible for the site-specific selection of a particular ISCO system and the associated design and operation of the system.
- The contributions of ESTCP Project ER-0623 along with others will help establish a standard of practice for ISCO.

# ISCO Screening

## 5. What ISCO options are available?

Oxidants and their respective activation approaches must first be screened based on their ability to degrade the COCs at a particular site. Contaminant treatability can vary not only by oxidant, but also by activation approach. Certain activation approaches may or may not work well within a site's baseline geochemical conditions. There is a wide array of delivery options for ISCO. Different delivery options tend to work best for specific oxidants and under different site conditions. It is important to match the delivery approach with the oxidant type and with the site hydrogeology and geochemical conditions. There is not one oxidant or delivery approach that works best under all COC, hydrogeology, and biogeochemistry conditions.

### Oxidants & activation:

- Permanganate
- Catalyzed hydrogen peroxide
  - Natural iron, chelated-iron, and iron + acidic pH
- Activated persulfate
  - Heat, hydrogen peroxide, chelated-iron, and alkaline pH
- Ozone
- Percarbonate
- Peroxone

### Oxidant delivery methods:

Injection wells and direct-push probes are most commonly used to deliver oxidants into contaminated groundwater. The table to the right shows the frequency of use of different delivery methods used for ISCO at 181 sites.

| Delivery Method (n = 181) | % |
|---|---|
| Injection Wells | 40 |
| Direct Push | 23 |
| Sparge Points (ozone) | 14 |
| Infiltration | 10 |
| Injectors | 7 |
| Recirculation | 7 |
| Fracturing | 6 |
| Mechanical Mixing | 2 |
| Horizontal Wells | 1 |

Note: Data in this table are based on DISCO. Multiple delivery methods were used at some sites.

### Effective delivery within a target treatment zone:

- Effective delivery requires injection of oxidant into the subsurface (e.g., via a well or probe) and transport throughout a TTZ (e.g., by advection, dispersion, diffusion).
  - Care needs to be taken to ensure that the injection well or probe design and operation avoid excessive loss in hydraulic capacity during a planned ISCO operation.
  - Displacement of contaminated groundwater may occur as a result of fluid injection into the subsurface. However, it can be minimized by properly designed injection regimes and well networks, or use of recirculation systems.
  - ISCO can be designed to rely on post-injection oxidant migration (e.g., by advection or 'drift') to achieve transport into access-limited areas. However, such migration can be limited by rapid oxidant species reactions with natural organic matter and reduced minerals.
- Delivery challenges can occur in TTZs with low permeability media (LPM), high heterogeneity, or DNAPL. Special ISCO designs can help overcome some limitations.
  - A $K_{sat}$ of $1 \times 10^{-4}$ cm/sec (0.28 ft/day) is considered a lower limit for standard injection without the use of enabling technologies such as soil mixing or hydraulic fracturing.
  - TTZs with high physical heterogeneity will typically require detailed characterization, spatially targeted oxidant delivery and multiple injection events.
  - When permanganate is used to treat a TTZ with appreciable DNAPL mass, the reaction product, $MnO_2$, can form a film or crust at the DNAPL-water interface. This can inhibit mass transfer and limit further DNAPL depletion. This can be managed to some degree by system design and operation (e.g., use of lower concentrations of oxidant delivered at a higher velocity).

# 6. What are key characterization needs for ISCO?

To be effective, all in situ treatment technologies require a sound conceptual site model (CSM) and a set of reasonably achievable treatment goals. ISCO requires the same general level of understanding necessary to select, design, and implement any in situ treatment technology, with additional focus on subsurface biogeochemistry, including:

- Oxidation-reduction potential (can provide insight into oxidant persistence)
- Reactivity of subsurface media with an oxidant (can control oxidant depletion over time)
- pH and alkalinity (can influence oxidation chemistry and free radical scavenging)
- Presence of redox-sensitive metals from mineralogy/geology, dissolved metals data, or site history (can help assess potential for post-treatment toxicity, e.g., Cr)

Much of this needed characterization information is immediately available in existing site documents and files (e.g., RCRA, CERCLA, State programs, etc.)

Because of the frequency of implementing MNA at sites for post-ISCO polishing, it is prudent to collect – before and after ISCO implementation – MNA parameters (e.g., nitrate, iron, sulfate/sulfide, methane, ethene, ethane, carbon dioxide, chloride, hydrogen, volatile fatty acids, pH, temperature, etc.) along with microbiological data using molecular biology tools (e.g., DNA analysis, lipid analysis).

# 7. Where does ISCO work best?

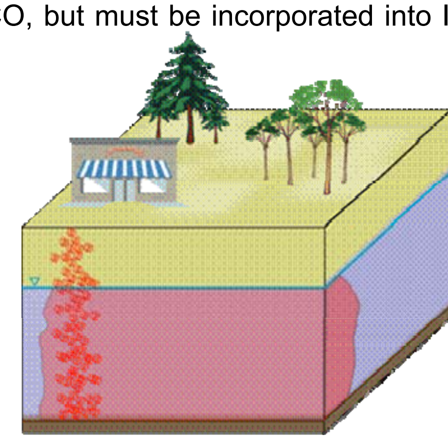
Like nearly all in situ technologies, ISCO is most effective in a target treatment zone (TTZ) that is permeable and has a relatively low degree of heterogeneity. Prospective target zones will often be identified in existing documents and data for the site (e.g., geologic cross-sections, stratigraphic representations, etc.). Conditions that tend to be well-suited to ISCO generally include:

- Moderate saturated hydraulic conductivities (e.g., $K_{sat} \geq 1 \times 10^{-4}$ cm/s)
- Low natural organic matter content (e.g., < 0.1 dry wt.%)
- Low contents of reduced metals that are redox-sensitive

Most of the common organic contaminants can be destroyed by one or more of the oxidants. The most frequently treated contaminants include chloroethenes (e.g., PCE and TCE) and fuel hydrocarbons (e.g., BTEX). Compared to NAPL, contaminants that are dissolved in groundwater or sorbed to soil or aquifer solids are more amenable to ISCO. NAPL can be addressed when treatment goals are realistic (e.g., mass reduction), however treatment to MCLs cannot be expected. Site features including lower permeability media, fractured bedrock, NAPL, or co-contaminant mixtures, do not preclude ISCO, but must be incorporated into ISCO design and performance goal setting.

ISCO tends to work well at sites where an oxidant can be delivered throughout a target treatment zone and persist during reaction with the target COCs.

Homogeneous, permeable groundwater zones exemplify well-suited conditions where adequate contact between an oxidant and contaminants is readily achievable using available delivery approaches.



# 8. What conditions are challenging for ISCO?

Site conditions that tend to be challenging for effective application of ISCO include those conditions that are challenging for most in situ technologies. For ISCO, key challenges are associated with:

- Strongly reducing conditions which exert high demand for some oxidants (e.g., highly reducing conditions, high organic matter, carbonates, etc.)
- Significant NAPL mass – particularly if there are extensive pools or mass trapped in zones of fractured rock
- Stringent treatment goals (i.e., goals that cannot be met by most treatment technologies) set for difficult site geology and contaminant conditions (e.g., treatment to MCLs in NAPL source zones located in a heterogeneous region of the subsurface)

> Often those conditions that challenge ISCO as a stand-alone technology can be overcome through an ISCO treatment train approach (e.g., ISCO followed by MNA).

# 9. Can ISCO be used in combination with other remedies?

Treatment of contaminants by other remediation techniques in conjunction with ISCO should be considered at all sites except those where ISCO is clearly capable of achieving clean-up goals as a stand-alone, cost-effectively remedy. Pre-ISCO COC mass recovery (e.g., by free product recovery) and/or post-ISCO polishing (e.g., ERD or MNA) can often increase the likelihood of meeting clean up goals and potentially reduce treatment times and costs.

**Using ISCO in a treatment train:**

Many other remedies are suitable for combining with ISCO, though their particular interactions with ISCO should be carefully evaluated.

Selection of remedies to combine with ISCO is normally based on

- Typical factors specific to the other remedial options
  - Contaminant susceptibility
  - Mass distribution
  - Site hydrogeology
  - Geochemistry
- Consideration of potential interactions
  - Reactions between chemical treatment reagents
  - Hydrologic impacts of treatment
  - Effect of pre-treatment residuals on follow-up ISCO treatment

**Questions related to combining ISCO with ERD or MNA methods:**

- Will the oxidant sterilize the soil and prevent post-ISCO microbial degradation of contaminants? ….. NO!
- Can ISCO byproducts inhibit or enhance bioprocesses? ….. BOTH!

Bioprocesses are likely to be disrupted over the short-term in the zone where oxidant is delivered, but rebound of microbial activity after active ISCO ends can be expected. The extent and duration of disruption depends on the oxidant concentration, exposure duration, and other site-specific factors such as pre-ISCO microbial conditions controlled by the dominant redox processes.

# ISCO Conceptual Design

## 10. How are ISCO systems designed?

If ISCO is selected as a viable alternative for a particular site, a site-specific design must be completed. The design of an ISCO system normally begins with the review of existing site data, subsequently followed by the completion of a conceptual design where key system attributes are explored and options are compared. For example, choices must be made concerning the oxidant concentration and volume to be delivered to a TTZ by a particular delivery method. The conceptual design can be used to examine ISCO system costs and key factors affecting their magnitude.

To assist developing conceptual designs as well as subsequent detailed designs, decision aids and computational tools are available (see ISCO Spreadsheet Design Tool). These can enable proper design of an ISCO system for a given site to achieve a desired performance.

**ISCO system design support:**

Design of an ISCO system can be enabled using a variety of decision aids and computational tools including:

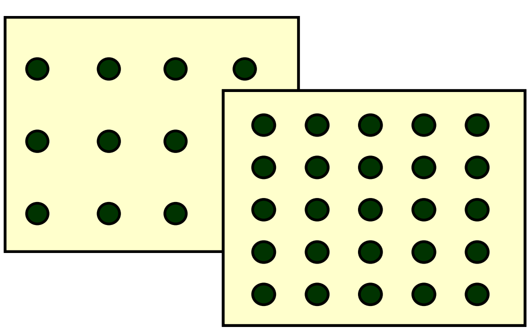
- Decision diagrams illustrating typical steps and procedures
- Tools for key design steps and decision points
  - Science-based text
  - Look-up tables
  - Spreadsheet calculators
  - Models (analytical and numerical)
    - General groundwater flow and transport models
    - ISCO specific models and design simulators

## 11. How many injection points are used?

Delivery of an oxidant into a groundwater TTZ is usually conducted using a network of injection wells or probes. The number of oxidant injection points is determined in the ISCO Conceptual Design process and depends on site-specific factors and design features, including:

- Presence of man-made structures (e.g., utilities)
- Oxidant type and reaction processes
- Oxidant delivery concentration and volume
- Delivery duration and rate
- Hydraulic conductivity
- Porosity
- Heterogeneity
- Contaminant mass and its distribution
- Areal extent of contamination

A typical ROI may range from about 5 to 15 feet per delivery point (e.g., for a probe or well injection), depending on the oxidant type and other site and design conditions. Injections may be performed at multiple depths suitable for site lithology and contaminant mass distribution.



The wider spacing shown in the top left is more appropriate where oxidant is less reactive with subsurface media (e.g., permanganate at a site with low natural organic matter and reduced minerals), higher porosity with low to moderate heterogeneity, and simpler contaminant mass distribution.

The closer spacing on the bottom right is more typical of a highly reactive oxidant (e.g., CHP) that is delivered rapidly for a short duration. It also may be typical of a site with greater heterogeneity, lower porosity, and/or complex contaminant distribution.

# 12. How many injection events are needed?

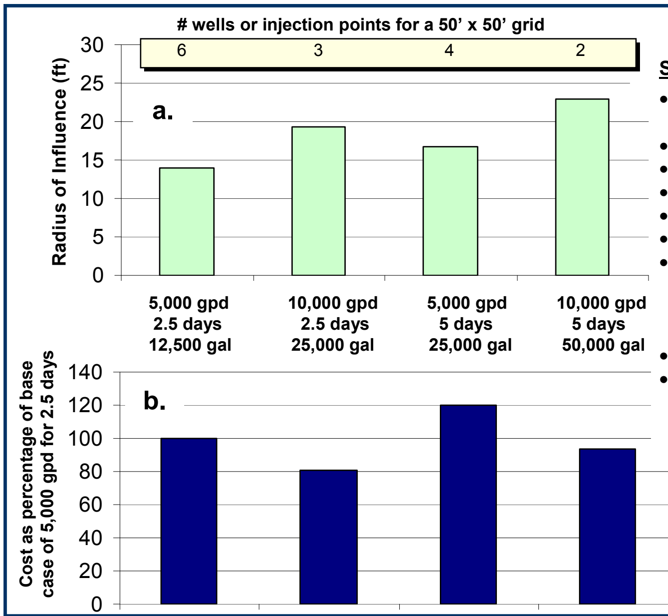
> The simple answer to the question of how many injection events are typically required is:
>
> ***Two or more!***

ISCO frequently requires the use of 2 or even 3 injection events at the same locations or at previously untreated locations. The average number of injections for sites for which case histories were reviewed was about 3. A survey of remediation professionals revealed that out of 66 respondents, 78% reported that 2 or more injection rounds were typical for ISCO applied to dissolved plumes in sandy media, and 89% reported that 2 or more injections were their average experience for source zones in sandy media (Vironex 2006). An "Observational Method", where detailed monitoring results collected after an initial injection are used to guide subsequent injections, is recommended.

# 13. How much oxidant solution should be delivered?

The tendency has been to inject just a fraction of a pore volume (PV) of oxidant solution at high concentration into a targeted zone, and to rely on advection, dispersion, or diffusion of oxidant as a means to transport it throughout the remainder of the treatment zone. However, research and experience have shown that treatment can be enhanced by increasing the volume of oxidant solution since it can result in an increased ROI and the need for fewer injection points per site (e.g., graph a. below) which in turn, can result in lower overall project costs (graph b.). Increasing the volume by increasing injection rate where feasible is more effective than increasing duration. When injected at a higher rate, less oxidant reacts nonproductively within the subsurface. The injection rate and volume is a balancing act based on soil fluid dynamics and treatment goals.

- Based on a review of field case histories
  - The average injected volume of oxidant solution (based on 68 sites) = 0.10 PV
  - PCE and TCE sites with > 90% concentration reduction: average injected volume = 0.50 PV
  - PCE and TCE sites with < 90% concentration reduction: average injected volume = 0.24 PV
- Survey of professionals (Vironex 2006)
  - The average injected volume specified in ISCO designs is 0.10 to 0.30 PV




**ISCO Design Simulations***

<u>**Simulation conditions:**</u>

- Target conc. at ROI = 500 mg/L $MnO_4^-$ for 4 days
- Thickness of treatment zone = 10 ft
- Porosity = 0.3
- Longitudinal dispersivity = 2.0 ft/day
- Hydraulic conductivity = 15 ft/d
- Soil bulk density = 1.6 kg/L
- Oxidant demand = 1 g/kg
  - o Fraction instantaneous = 0.3
  - o Slow oxidant demand rate ($2^{nd}$ order) = 0.02 L/mmol-d
- Oxidant level injected = 5,000 mg/L
- Injection ROI overlap = 25%

*Injection rate and duration varied to vary injection volume*

* Simulatons performed with a design tool developed for the ISCO TPM. Results shown are specific to the conditions simulated, but the trend appears consistent for varied conditions.

# 14. Why perform lab treatability tests?

Laboratory testing is typically conducted because the existing data set is inadequate for design and/or site conditions are complex enough that standard protocols (i.e., existing simplified design tools) do not apply. The goal is normally to improve the understanding of system reaction chemistry to increase the confidence of estimates of treatment effectiveness and ISCO costs for a specific site.

**ISCO designs may require lab testing to determine:**

- Oxidant demand / persistence (by natural media interaction with oxidant)
  - Oxidant demand data are needed for most permanganate sites (24-48 hr bench test)
- Oxidant's expected radius of influence (ROI)
  - The rate of oxidant demand can be incorporated into an estimate of injected solution ROI to estimate how far the oxidant itself will be expected to reach while it is depleted in the subsurface
- Contaminant or co-contaminant degradability
- Contaminant desorption/ dissolution
- Potential for intermediates and/or byproducts, or for metals solubilization
- Optimized oxidant dose or activation approach

**Questions that testing can help provide insight into:**

*Can ISCO mobilize metals?*
- Yes; however they typically occur primarily in the target treatment zone and attenuate quickly

*What other effects may ISCO have?*
- Increase or decrease in pH, increased solids and gas production, elevated temperatures, increased ORP, increased DO, increased specific conductance, secondary geochemical; effects (e.g., elevated manganese or sulfate)

*How do you evaluate potential impacts?*
- Laboratory batch reaction test to evaluate "worst case scenario" possibilities
- Flow-through or field pilot tests can confirm or invalidate

**How do you evaluate and optimize system reaction chemistry?**

Batch reaction tests:
- Range of conditions – oxidant type, oxidant concentration/dose, oxidant activation method
- Use site media – soil and groundwater from each distinct lithologic zone
- Measure contaminant, oxidant, byproducts, intermediates, etc. (as needed) over time

Flow-through reaction tests:
- To understand added complexities – oxidant transport, COC dissolution, desorption, etc.

**Considerations for evaluating batch test results:**

Lab systems can have turbulent mixing and achieve 100% contact between soil, water, contaminant, and oxidant, AND no dilution or dispersion, therefore:

- Contaminant destruction results = *BEST case scenario*
- Oxidant depletion rate and extent = *WORST case scenario*
- Byproduct/intermediate generation = *WORST case scenario*

# 15. Why perform field pilot tests?

Field pilot testing is typically conducted to evaluate scale-dependent processes impacting ISCO design, such as:

- Ability of the formation to accept a volume of oxidant or rate of delivery.
- Impact of heterogeneities on oxidant distribution (e.g., via tracer test).
- Radius of influence of oxidant.
- Subsurface biogeochemical responses.

Field pilot testing can help to assess contaminant rebound potential; however it is important that migration from upgradient contaminated zones is NOT considered rebound. It may also be possible to get a sense for overall treatment effectiveness, but site heterogeneities and uncertainties associated with upscaling system design should be considered. Additionally, it is *inappropriate* to analyze for contaminant concentrations while oxidant remains at the monitoring location.

# 16. What are the advantages and disadvantages of lab and field testing?

The primary advantage of lab-scale testing is that extensive data can be collected relatively efficiently and cost-effectively. The primary disadvantage is managing issues of scale-up and extrapolation to the field in situ.

The primary advantages of on-site pilot testing include the ability to collect data at the field scale and to evaluate oxidant deliverability. The primary disadvantage is the greater cost and time associated with field scale data collection.

| | Used to Evaluate | Advantages | Disadvantages |
|---|---|---|---|
| **Laboratory batch** | • Appropriate oxidant and activation method<br>• Optimized oxidant dose<br>• Oxidant persistence<br>• Contaminant degradability (idealized)<br>• Contaminant desorption / dissolution (idealized)<br>• Intermediates / byproducts generation<br>• Geochemical impacts | • Initial assessment of ISCO applicability<br>• Comparison of reaction chemistries<br>• Ability to evaluate wide range of conditions economically<br>• Extensive data collected efficiently and cost-effectively | • Managing issues of scale up and extrapolation of results from bench top to in situ |
| **Laboratory flow-through** | • Oxidant persistence and deliverability<br>• Contaminant degradability<br>• Contaminant desorption / dissolution<br>• Intermediates / byproducts generation<br>• Geochemical impacts | • Extensive data collected with moderate efficiency and cost-effectiveness<br>• Transport / deliverability factors can be evaluated | • Managing issues of scale up and extrapolation of results from bench top to in situ |
| **Field pilot** | • Oxidant persistence and deliverability<br>• Contaminant degradability<br>• Intermediates / byproducts generation<br>• Biogeochemical impacts<br>• Oxidant radius of influence<br>• Impacts of heterogeneities<br>• Potential for rebound | • Ability to collect data at the field scale<br>• Ability to evaluate oxidant deliverability<br>• Greater certainty in full scale performance and cost | • Greater cost and time associated with field scale data collection |

**Typical cost and time required:**

Laboratory batch tests can cost up to about \$5K for simple oxidant demand tests (i.e., permanganate) and about \$5K-50K for others; laboratory flow-through or pilot testing can be about \$20K-100K (depending on scale and complexity); and field pilot tests can be about \$50K-300K (depending on scale and complexity). Most laboratory tests span several weeks to months while pilot scale tests, including post-treatment monitoring, can take up to a year depending on the size/scale of the site and complexity of the subsurface and system design.

# 17. What does an ISCO project cost?

Describing a typical cost for an ISCO project is very difficult and prone to errors due to cost-dependencies on site-specific conditions, design details, and performance goals, as well as wide variability in unit costs across the U.S.

According to a review of case histories for over 200 ISCO field applications, the median cost was about $220K per project. On a unit cost basis, the median cost for performing ISCO is $94/yd$^3$. The costs reported appeared to depend on the COCs being treated (BTEX sites tend to have a lower mean cost), hydrogeology (increasing complexity translates to increasing cost), and contaminant mass present (e.g., DNAPL sites are more costly than those with only dissolved and sorbed phase contamination). Interestingly, the type of oxidant used for ISCO does not dictate cost when the appropriate oxidant and delivery approach are selected for a site. In other words, use of one oxidant is not inherently more or less expensive than another.

Average costs for ISCO by unit volume treated may continue to decrease over time, presumably due to increased understanding of appropriate implementation measures.

Reported cost of ISCO field applications based on a review of ISCO case histories.

| | Total Cost ($) | Unit Cost ($/yd$^3$) |
|---|---|---|
| Minimum | 15,000 | 2 |
| Quartile 1 | 141,500 | 36 |
| Median | 222,000 | 94 |
| Quartile 3 | 395,000 | 242 |
| Maximum | 1,670,000 | 4725 |
| | n = 55 | n = 33 |

# ISCO Detailed Design and Planning

## 18. Are there regulatory requirements that can hinder the application of ISCO?

ISCO has been used for remediation of contaminated groundwater in every state of the U.S. and several countries worldwide. The permitting process varies from state to state and includes requirements typical for projects using in situ remediation technologies as well as a few requirements specific to ISCO. The Interstate Technology & Regulatory Council (ITRC) document "Technical and Regulatory Guidance for In Situ Chemical Oxidation for Contaminated Soil and Groundwater, Second Edition" (January 2005) provides detailed information regarding typical regulatory barriers, along with examples highlighting the permitting process. Relevant regulations and regulatory issues may include Underground Injection Control, state approvals for materials (e.g., metals content of permanganate solution), RCRA Hazardous Waste TSD (Treatment, Storage, and Disposal) permitting for ex-situ mixing and hazardous waste generation, CERCLA "release" or "process" definition, EPCRA reporting, secondary containment, OSHA requirements, potential exacerbation of indoor air exposure, and impacts to secondary water quality standards (e.g., manganese, sulfate, etc.).

## 19. Are there special safety precautions with ISCO?

Oxidants are relatively safe chemicals when handled and stored properly by trained personnel. However, accidents have occurred when ISCO was implemented without appropriate caution and attention to health and safety. The primary hazards associated with oxidant use are dermal exposure effects, gas and heat generation, and the potential for uncontrolled reaction through improper storage. It is important to consider the hazards of dusts of solid phase oxidants (e.g., $KMnO_4$ and $Na_2S_2O_8$), as well as electrical hazards associated with oxidant generation on site (e.g., ozone). Oxidant reactions can be vigorous and exothermic and can result in significant generation of gas and heat, which must be considered in developing site safety and health plans.

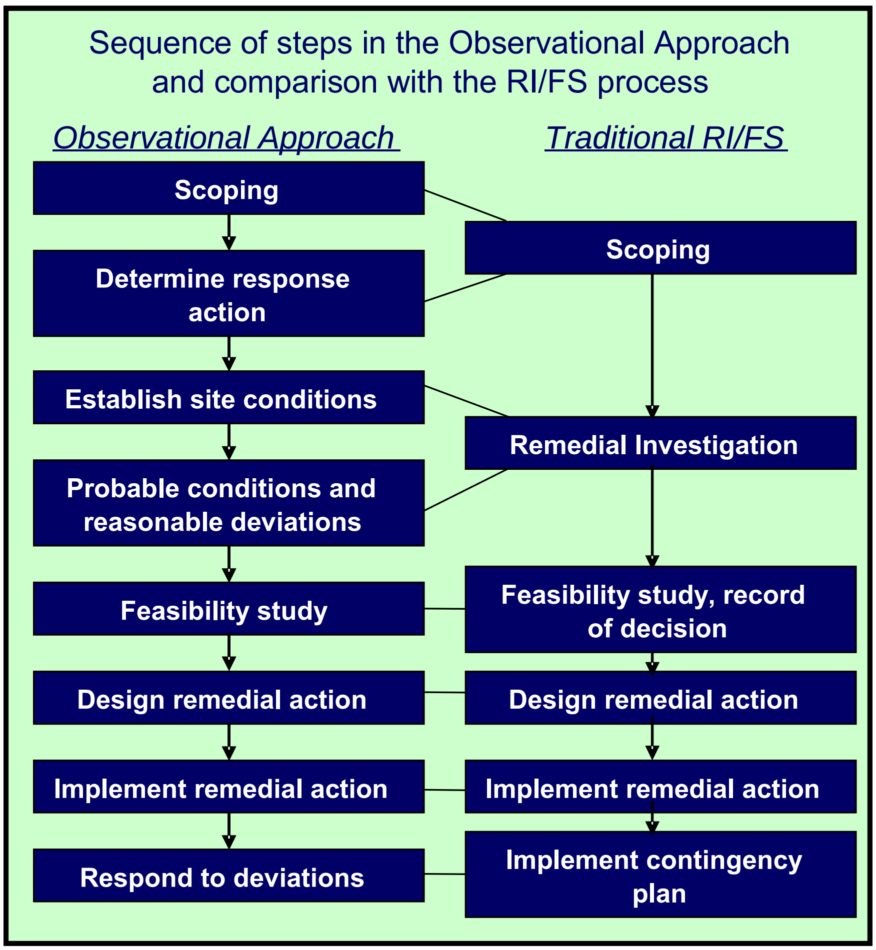
Chemical manufacturers and vendors should be consulted for oxidant-specific health and safety precautions and protection measures. Engineering controls and appropriate personal protective equipment must be employed in handling and mixing oxidants. Site health and safety plans must include safety precautions and appropriate training for the specific oxidant(s) to be used on site, including oxidant activators such as acids or bases.

> Oxidant surfacing or day-lighting onto the ground surface is possible, particularly when using pressurized probe injection into tight formations where oxidant may travel up the outside of the probe to the surface if the formation offers greater resistance than the path to the surface.

# 20. How is ISCO optimized during implementation?

The effectiveness of ISCO can be optimized in real time by applying an Observational Method throughout technology screening, design, implementation, and monitoring. The goal of the Observational Method is to integrate performance monitoring results and decision logic real-time, allowing for modification "as you go". This type of method relies on understanding the uncertainties associated with the CSM and on planning ahead for reasonable bounds of conditions that may occur at the site.

> As stated earlier, most sites will require 2 to 3 injections of an oxidant solution. An Observational Method can be used to help guide/focus any injections following the initial injection to improve cost-effectiveness per injection event. In particular, monitoring data can be assessed to focus subsequent injections on untreated zones where unacceptably high contaminant concentrations remain.




> The use of techniques such as direct push technologies and in situ sensors with data loggers, along with the development of GIS and geostatistical packages used in the field to analyze data, have dramatically improved the ability to apply an Observational Method.

## 21. What are appropriate milestones, metrics, and endpoints for ISCO?

Preparation of an ISCO operation plan and establishing clear operational and/or performance objectives and endpoints is important to maintain a proactive and adaptive ISCO project. The intent of the operation plan is to lay out expectations for the ISCO treatment and obtain project team and regulator consensus on the approach and goals prior to ISCO implementation. The implementation timeframe should address the minimum amount of time needed for the treatment zone to return to equilibrium after ISCO treatment (site-specific). It is only after subsurface re-equilibration that ISCO effectiveness can be determined.

Example endpoints may include completion of oxidant delivery to the target treatment zone and oxidant persistence for a minimum amount of time needed for treatment as indicated by laboratory or field testing. Milestones can be established using laboratory or field testing data.

Metrics should be established to measure achievement of the endpoints. For example, a concentration of permanganate greater than 500 mg/L throughout the target treatment zone may be sufficient to demonstrate completion of oxidant delivery.

Endpoint definition is important to limit the extent of ISCO treatments such that perpetual injection cycles are avoided if treatment goals are not achieved. Operational endpoints can be:

- Definitive, such as a maximum of three injections will be completed to achieve the maximum practical extent of contaminant treatment, or
- Procedural, such as ISCO will be applied until contaminant concentrations in groundwater reach an asymptotic level.

# ISCO Implementation and Performance Monitoring

## 22. What should be monitored for an ISCO project?

Monitoring of ISCO includes operational monitoring for process control (e.g., oxidant concentrations, delivery rates, injection pressure, volume injected) and treatment performance monitoring (for regulatory compliance and site closure). Monitoring can include collection of baseline data before ISCO is implemented. The monitoring program is designed to evaluate/confirm appropriate oxidant injection concentrations and volumes, oxidant distribution/radius of influence, and contaminant destruction. It is also designed to detect and enable management of ISCO effects such as gas generation and changes in temperature, subsurface pressure and changing water table levels. Specific analytical methodology prescribed by the regulatory program under which ISCO is being administered should be followed. Monitoring plans should be dynamic and adaptive and use real-time monitoring during oxidant delivery to facilitate optimization.

| Parameter | $MnO_4^-$ | CHP | $S_2O_8^-$ | Ozone |
|---|---|---|---|---|
| Oxidant | D, T | D, T | D, T | D, T |
| Color | D | | | |
| pH | T | D, T | D, T | D |
| Oxidation / reduction potential[1] | D, T | D, T | D, T | D, T |
| Temperature | | D | | D |
| Alkalinity | | D | | T |
| Vadose offgas ($CO_2$, $O_2$, VOC, ozone) | | D | | D |
| Dissolved oxygen | | D, T | T | D, T |
| Specific conductivity[1] | D, T | | D, T | |
| Sodium | | | D | |
| Sulfate | | | D, T | |
| Dissolved Iron (ideally differentiating $Fe^{2+}$ and $Fe^{3+}$) | | D | D | |
| Injection pressure | D | D | D | D |
| Injection flow rate[1] | D | D | D | D |
| Water level | D | D | D | D |
| Injectate concentration | D | D | D | D |
| Fluid pressure[1] | D | D | D | D |
| Tracers | D | D | D | D |
| COCs | T | T | T | T |
| Chloride (for chlorinated compounds) | T | T | T | T |
| Manganese | T | | | |
| Geochemcial indicators for NA (nitrate, microbes)[2] | T | T | T | T |
| Redox-sensitive metals (e.g., Cr) | T | T | T | T |

D = Injection / delivery / operation performance monitoring; T = Treatment performance monitoring

CHP = catalyzed hydrogen peroxide; NA = Natural attenuation

[1] Suitable to use for real-time data to optimize the ISCO treatment process

[2] Suitable for systems utilizing a coupled approach with a biological component

The appropriate number/spacing of monitoring wells depends on site-specific objectives and regulatory requirements. The monitoring network should be designed to achieve the data objectives stated for the ISCO project. For example, an adequate number of wells should be sited within and around the target treatment zone to demonstrate uniform oxidant delivery both near and at the farthest reaches of the oxidant radius of influence. If statistical methods will be used to determine post-treatment conditions, then an adequate number of samples should be collected to perform a valid analysis.

It is important to understand the differences in oxidant distribution and injection fluid distribution when using indicators of oxidant distribution. Due to reaction, the oxidant will not move as far as the delivery solution, and this discrepancy should be considered in monitoring frequency and time between measurements. Another consideration is that, due to preferential flow resulting from heterogeneities, observing the oxidant at a monitoring location some distance from the injection point does not necessarily mean that the entire saturated thickness of the formation was contacted between the oxidant delivery and monitoring points.

## 23. What is rebound? Is it a problem?

There is no universally accepted definition of contaminant rebound. It is defined operationally here as an increase in aqueous phase COC concentrations that occurs after active ISCO operations have ended and following an initial reduction in concentration that resulted from the ISCO application. This type of rebound is a common occurrence at ISCO sites. Because ISCO typically involves two or more injection events, the information provided by rebound measurements can be valuable to the design of follow-on oxidant injection events.

**Primary causes of rebound:**

(1) COCs enter the TTZ after ISCO is completed (e.g., by movement from an upgradient location or continued migration from an associated source).

(2) Contaminant mass in the TTZ remains untreated by the ISCO system.

(3) ISCO affects contaminant partitioning by altering porous media properties that govern partitioning (e.g., destroying organic carbon, modifying surface area) which leads to a greater % of the contaminant mass being in the dissolved phase within the TTZ.

The first cause (1) involving migration from upgradient contaminated areas is NOT considered true rebound. This apparent rebound may be the result of an inadequate CSM and improper selection of a TTZ and/or ISCO system design with deficient hydraulic control during and following ISCO.

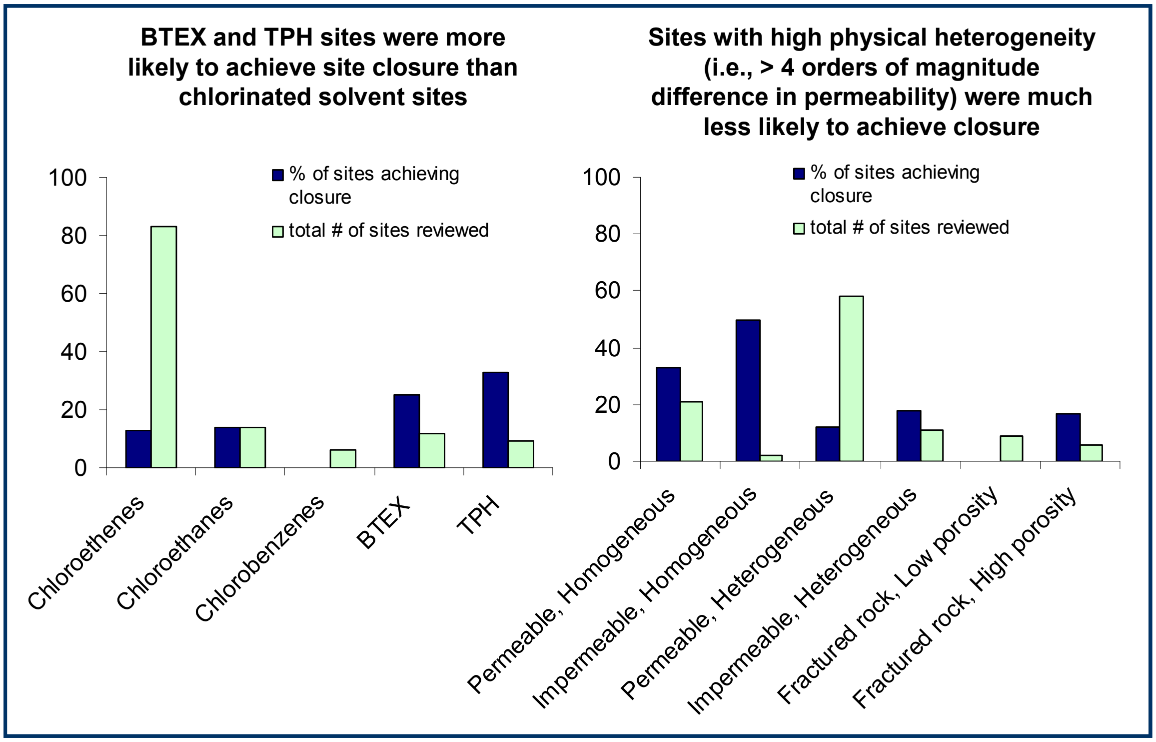
True rebound may be caused by (2) which can result from poor oxidant distribution and contact with the contaminants, the short-lived nature of some oxidants with respect to typical remediation timeframes (i.e., oxidant is depleted before all contaminant mass transfer can occur), or the presence of untreated NAPL/sorbed contaminant that can dissolve/diffuse to the aqueous phase.

True rebound may also be caused by (3) which can benefit eventual contaminant destruction due to potential for increased accessibility of contaminant to oxidants.

True rebound can occur and it should be anticipated with ISCO. It is not necessarily an indication that ISCO was inappropriate for a site or improperly applied.

## 24. How successful has ISCO been at achieving site closure?

Of 74 full-scale completed sites with enough performance data available for review, 24% of these sites have achieved closure. This value may be an underestimate, as some sites may have achieved closure given the time that has passed since the respective project documents were published. Also, only those sites for which closure could be directly verified through site regulators were included in this statistic. Furthermore, sites may have alternative endpoints such as: 1) transition from active treatment (e.g., ISCO) to a more passive technology like MNA or in situ bioremediation, 2) transition to land use controls, or 3) transition to long-term monitoring. ISCO itself is not often intended to completely clean up and close a site, but is commonly a component of a range of these different site closure strategies. These alternative endpoints may not represent true site closure, but they do allow site owners to shift remediation focus and costs to lower monitoring and management activities instead of capital intensive and expensive, aggressive source treatment. Transition to MNA or long-term monitoring typically means "remedy-in-place" (RIP) has been achieved, which can be an important milestone for site management.




Only 8% of sites with contaminant present at concentrations > 1% of solubility (e.g., NAPL potentially present) achieved site closure (n = 60), whereas 25% of sites with concentrations < 1% of solubility achieved closure (n = 39).

Results are dependent on regulatory context: States vary in their requirements for closure; therefore some sites achieving closure may be at the point of reaching MCLs, whereas others may simply demonstrate a stable plume with no free product.

# Additional Information

## 25. Where can I find more information on the principles and practices of ISCO?

Information regarding the principles and practices of ISCO can be obtained through an array of published literature including journal articles, conference papers, reports, and reference books. As part of the ESTCP ER-0623 project, a critical review of the literature has been completed (see S1. Literature Summary and S2. Annotated Literature Review). Another source of information is the compilation and analysis of ISCO field applications (see Database of Field Applications and Experiences with ISCO Sites).

A few references are listed below that the reader of this FAQ may wish to refer to include those that provide a description of ISCO principles and practices as well as those with guidance regarding field applications:


- Environmental Security Technology Certification Program (ESTCP) (1999). Technology Status Review: In Situ Oxidation. http://www.estcp.org.
- Huling, S.G., Pivetz, B.E. (2006). "Engineering Issue: In-Situ Chemical Oxidation." Office of Research and Development, U.S. Environmental Protection Agency. 58 pg.
- In Situ Chemical Oxidation for Remediation of Contaminated Groundwater: Summary Proceedings of an ISCO Technology Practices Workshop (2008). Proceedings of a workshop convened at the Colorado School of Mines, Golden, CO, March 7-8, 2007. (see S.3 ISCO Technology Workshop Proceedings). Also available through the DoD SERDP/ESTCP Program Office, Washington, D.C.
- Interstate Technology & Regulatory Council (ITRC) (2005). Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd Edition (ISCO-2). Washington DC. http://www.itrcweb.org/Documents/ISCO-2.pdf.
- Krembs, F.J. (2008). Critical Analysis of the Application of In Situ Chemical Oxidation for the Remediation of Contaminated Groundwater. M.S. Thesis submitted to the Colorado School of Mines, Environmental Science and Engineering.
- Siegrist R.L., M.A. Urynowicz, O.R. West, M.L. Crimi, K.S. Lowe (2001). Principles and Practices of In Situ Chemical Oxidation Using Permanganate. Battelle Press, Columbus Ohio. 336 pg.
- United States Environmental Protection Agency (EPA) (1998). In situ remediation technology: in situ chemical oxidation. EPA 542-R-98-008. Office of Solid Waste and Emergency Response. Washington, D.C.
- Vironex. (2006). "Vironex In-Situ Chemical Oxidation National Survey." http://www.vironex.com/pages/support_chem_ox_survey.html.


In addition to the current base of information available through the published literature and analysis of case studies, ISCO innovations and advancements are continuing and new information will be available over time. For example, the DoD through its SERDP and ESTCP programs has recently funded or is currently funding a number of projects that are focused on ISCO. ESTCP Project ER-0623 is one of those. Information regarding other SERDP/ESTCP projects that are focused on ISCO can be obtained from the SERDP/ESTCP websites at www.serdp.org or www.estcp.org.

Finally, general and detailed information about ISCO can be obtained from design professionals, chemical company personnel, and others who possess know-how and understanding through their substantial experience with ISCO for groundwater remediation.

# Acronyms and Abbreviations

| | | |
|---|---|---|
| ACLs | - | alternative concentration limits |
| BTEX | - | benzene, toluene, ethyl benzene, xylenes |
| CERCLA | - | Comprehensive Environmental Responsibility, Compensation and Liability Act |
| CHP | - | catalyzed hydrogen peroxide; catalyzed hydrogen peroxide propagations |
| COC | - | contaminants of concern |
| CSM | - | conceptual site model |
| DISCO | - | database for ISCO developed under ESTCP Project ER-0623 |
| DNAPL | - | dense nonaqueous phase liquid |
| DoD | - | Department of Defense |
| EPCRA | - | emergency planning and community right to know |
| ER-0623 | - | project number for this ESTCP project to develop an ISCO TPM |
| ERD | - | enhanced reductive dechlorination |
| ESTCP | - | Environmental Security Technology Certification Program |
| FAQ | - | Frequently Asked Questions |
| FS | - | feasibility study |
| $H_2O_2$ | - | hydrogen peroxide |
| ISCO | - | in situ chemical oxidation |
| $KMnO_4$ | - | potassium permanganate |
| Ksat | - | saturated hydraulic conductivity |
| MCL | - | maximum contaminant level |
| MNA | - | monitored natural attenuation |
| NA | - | natural attenuation |
| $Na_2S_2O_8$ | - | sodium persulfate |
| NAPL | - | nonaqueous phase liquid |
| NFECSD | - | Naval Facilities Engineering Command Southeast Division |
| NFESC | - | Naval Facilities Engineering Service Center |
| NOD | - | natural oxidant demand |
| $O_3$ | - | ozone |
| ORP | - | oxidation-reduction potential |
| OSHA | - | Occupational Safety and Health Administration |
| PAHs | - | polyaromatic hydrocarbons |
| PCE | - | perchlorothene, tetrachloroethene, or tetrachloroethylene |
| ppb | - | parts per billion |
| RCRA | - | Resource Conservation and Recovery Act |
| RI | - | remedial investigation |
| RIP | - | remedy in place |
| ROI | - | radius of influence |
| RPM | - | remedial project manager |
| SERDP | - | Strategic Environmental Research and Development Program |
| TCE | - | trichloroethene or trichloroethylene |
| TPH | - | total petroleum hydrocarbons |
| TPM | - | technology practices manual |
| TSD | - | treatment, storage and disposal |
| TTZ | - | target treatment zone |
| USEPA | - | U.S Environmental Protection Agency |
| VOC | - | volatile organic compound |